LEATHER REFUSE;

Its Value in Agriculture.

BY

J. B. LINDSEY, Ph. D.,

MASSACHUSETTS STATE EXPERIMENT STATION,

AMHERST.

W. F. HUMPHREY,
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LEATHER REFUSE—ITS VALUE IN AGRICULTURE.

BY J. B. LINDSEY.

First Paper.

During the past few years, claims have been made at various times that large quantities of leather shavings and the like have found their way into the so-called commercial fertilizers that are so widely used by the farmers of the United States. The writer has no means of knowing whether this claim is true or not. It should be the object of the fertilizer manufacturer to utilize all kinds of waste products that possess distinct manurial value. By so doing he not only benefits himself, but the farmer as well.

It was very early assumed from its chemical character, without any exact experiments upon which to base the assumption, that leather refuse would yield its nitrogen as plant food very slowly if at all.

Methods Employed to Make the Nitrogen Available to Growing Plants.

The first method suggested, so far as the writer has been able to ascertain, was that prescribed by F. O. Ward*, of England, in 1857, for turning to account woolen rags, wool, silk and leather clippings. The process as described was as follows: The refuse was introduced into an ordinary autoclave digester, and there kept for about three hours, surrounded by steam heated to a pressure of from three to five atmospheres. Wool required a higher temperature than leather, and silk than wool. The materials condensed a portion of the steam, and absorbed its heat. This joint action converted the animal matter into a friable substance, which,

* Report by the Juries of the International Exhibition, 1862. Reporter, A. W. Hoffman. Repertory of Patent Inventions, Aug. 1857, page 137.

however, still retained its original form and aspect. It was then ground fine, sifted, and bagged. "The details of the process, the fuel- and labor-saving arrangements that have been learned, point by point, by costly manufacturing experience cannot," says Ward, "with propriety be divulged." The final product is described as a dark colored powder. The nitrogen in the finished product is said to exist to a small extent, as ready formed ammonia, being in combination with ulmic and humic acids developed during the process. It was stated at the time, that this manufacturing process was carried on at large works on the Thames. The material for the most part was sold to manure manufacturers, who used it as an ingredient of their several fertilizing compounds, and it was "used by many farmers who are not aware of the fact." Ward says that "while this material is not as active as some other forms of organic nitrogen, it possessed distinct value as a fertilizer."*

Edw. Toynbec† in 1858, also described a process whereby leather and wool waste could be cooked in sulfuric acid, and be made more available as a fertilizer. He said "that to one centner of sulfuric acid, four or five centners of wool or leather waste could be added." The writer does not see how such a large amount of leather could be added to the acid, as will be shown further on. L. Meyer‡ speaks of dissolving all such refuse substances in warm sulfuric acid, and neutralizing the moist mass with bone.

A Lipowitz§ notes the fact that the Posner fertilizer factory utilizes all such kinds of waste, as have already been referred to.

Runge¶ speaks of rendering leather and wool more available, by dissolving them in a mixture of Glauber's salt and quick lime. This chemist manufactured a fertilizer upon a large scale from these materials.

Reichardt**describes his method of subjecting the leather refuse

*The writer does not know whether this process is still in operation in England, for utilizing the leather, wool, and silk wastes.

†Repertory of Patent Inventions 1858, p. 389; Jahresbericht Agric. Chem., 1859.

‡Jahresbericht Agric. Chem., 1859, 228.

§Allgem. Zeitung für deutsche Land. und Forstwirthe, 1859, 153.

¶Jahresbericht Agric. Chem., 1865.

**Zeitschrift für deutsche Landwirtschaft, 1865, 136. Jahresbericht Agric Chem., 1865.

to steam pressure, and then drying it quickly. After such a treatment he found 15.75 per cent. of the material to be soluble in boiling water, and that after standing for some time, 20 per cent. could be dissolved. By treating the dry leather that had been subjected to steam, with 20 to 40 per cent. sulfuric acid, he was enabled to dissolve from 22 to 29 per cent. of the leather in water. With a 5 per cent. solution of crystallized soda, 28.8 per cent. could be brought into solution. He therefore concluded that the best method was to subject the leather to the action of a weak soda solution.

Coignet's* method was reported in 1874 by H. Mangon. Briefly stated, it is as follows: The refuse material is placed in a room having a cubic area of 20 meters. Directly outside of the room is a coke oven, connected with a chimney that has an opening into the room containing the material to be treated. Into this chimney are conducted jets of steam, so that the room is heated from 150° to 160° C. for several hours by this moist chimney air. Under these conditions the leather swells somewhat, and becomes dark, brittle, and can easily be rubbed to a powder.

Storer† says, "It is evidently with reference to this process, that the statement has recently been made, that certain manufacturers of fertilizers at Paris devote themselves particularly to the preparation of torrefied wool, horn, leather, and even bone, the leather having first been steamed strongly to remove oil and gelatine."

L'Hote‡ describes a method whereby such waste material as wool, leather, etc., can be converted into sulfate of ammonia. He suggests dissolving the material in a ten per cent. solution of caustic soda in the cold. The substances will be partly dissolved, or their structure more or less destroyed. The jelly-like mass is then mixed with caustic lime till it becomes of a doughy consistency. It is then brought into iron retorts, and heated at first at as low a temperature as possible in order to prevent the dissociation of the ammonia, which is caught in sulfuric acid. After the gas has been nearly driven off, the retorts are subjected to red

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*Organ der Verein f. Rübenz. Industrie in Œster-Ungarn, 1874, 32. Jahresbericht Agric. Chem. 1873–1874, 37.

† *Agriculture* I., 382.

‡ Centralblatt für Agric. Chem. 5, 258. Illustrirte landw. Zeitung, 1874, No. 2, 18.

heat. At the end of the operation, a white powdery substance is left behind, consisting of carbonate of soda and caustic lime. By cooking this substance with water, caustic soda is formed and can be again utilized. By this method all the nitrogen is obtained. The resulting sulfate of ammonia is somewhat colored.

For utilizing leather Rümpler* suggests the following method: In lead or iron jacketed kettles, sulfuric acid of 50° B. is heated very hot, and leather stirred in till a dark brown fluid is obtained. This fluid is then used to dissolve the phosphate of lime. He remarks that "the nitrogen is saved, and without doubt is much more available from the fact that the tannin is destroyed."

Erhardt † suggests that such refuse material be slowly burned in closed ovens, and the gas collected in moist muck, till the latter becomes saturated. This muck mixed with superphosphate gave, he says, a quick acting manure.

Deherain‡ says that this leather refuse can be dissolved in sulfuric acid, and the excess of acid neutralized with phosphate of lime. In this way he claims a very active fertilizer can be obtained at a low cost.

The writer understands that this latter method has been in quite general use for many years by European manufacturers. Not only has leather been thus treated, but also a great variety of nitrogen-containing refuse materials. American manufacturers also subject various waste materials to the action of sulfuric acid, in order to render them more quickly available.

From the many methods suggested for the utilization of leather waste, it is evident that, in the older countries, especially England, France and Germany, this material after having been submitted to some mode of treatment, is quite generally used, to a greater or less degree, in the manufacture of commercial fertilizers.

Petermann § says, "that it is well-known that certain Belgian and French manufacturers use leather in their products, but that such goods contain, in addition, nitrogen in other forms, such as blood, horn meal, sulfate of ammonia and nitrate of soda." He further states that the "factories producing this material are numerous, and a considerable quantity is produced annually."

* Kaüfliche Düngestoffe. H. Rümpler, 1875 (Thaer Bibliothek).

† Jahresbericht Agric. Chem., 1880, 337.

‡ Deherain, *Chimie Agricole*, [1892], 624.

§ *Recherches de Chimie et Physiologie* [1886], 144.

Manurial Value of Prepared Leather Waste.

The different experiments made to prove the value of leather have been conducted either with untreated finely ground leather, with torrefied leather, or with leather steamed under pressure.

Three different methods have been used, in testing the agricultural value of leather: (a) by directly testing its fertilizing effect either in pot or plat experiments ; (b) by artificially digesting it with a pepsin solution ; (c) by noting the length of time required to nitrify it. The first method is by far the most interesting, and leads to direct results. The other two serve at least to confirm the results obtained by the first method.

(a) *Pot and Plat Experiments.*

Very early experiments are not to be found in the literature.

The first experiment recorded was made by Ladureau,* and lasted but a single season. He found that 2500 kilos. of torrefied leather yielded 30,100 kilos. of sugar beets, testing 8.83 per cent. of sugar, and 2500 kilos. of the same leather plus 200 hectolitres of lime gave 38,600 kilos. of beets, with 10.10 per cent. sugar. The same area of land without leather, yielded 20,000 kilos. of sugar beets testing 10.93 per cent. sugar. Petermann remarks on these results as follows : "In spite of the increased yield obtained by using the leather, the experiment was not a success financially and further, the beets produced with the aid of the leather were poorer in quality than those without it."

In 1880, Petermann † carried out a series of experiments with ground, steamed leather, to test its manurial value. It was very dry and brittle, and contained 7.51 per cent. of nitrogen and 0.81 per cent. of phosphoric anhydride soluble in hydrochloric acid.

The experiments were carried on in the plant house in pots, with oats ; in the garden, with the horse bean (*Vicia faba*) ; and in the field, with sugar beets.

I. Experiments with Oats in Pots.

Each test was made in duplicate. The soil was what might be called a sandy clay, each pot holding 4,000 grammes. The fertilizer was mixed with three-fourths of the soil of each pot. To the soil

* Annales Agron., 1878 ; *Loc. cit.*, 146.

† *Loc. cit.*, 144, Centralbl. Agric. Chem. **10**, 590.

in each pot were added 0.25 gramme of nitrogen, 0.30 gramme of phosphoric acid, and 0.20 gramme of potash.

RESULTS—AVERAGE OF THE DUPLICATES, EXPRESSED IN GRAMMES.

	Entire plant.	Straw.	Chaff.	Grain.
Unmanured	22.34	15.19	0.95	6.20
SERIES I.				
Nitrogen				
(a) Leather	34.85	26.65	1.25	6.95
(b) Dried blood	51.91	36.68	1.82	13.41
SERIES II.				
Nitrogen + Phosphoric Acid.				
(a) *Leather* + precipitated phosphate	39.93	31.28	1.15	7.50
(b) *Blood* + precipitated phosphate	51.97	36.45	1.91	13.61
SERIES III.				
Nitrogen + Phosphoric Acid + Potash.				
(a) Leather + precipitated phosphate + muriate of potash	A30.55	21.90	1.09	7.56
(b) Dried blood + precipitated phosphate + muriate of potash	37.40	29.65	1.82	15.93

In observing the results of the experiments, we notice especially with reference to the grain produced, that the leather did not increase the yield to any appreciable extent over that of the unfertilized pots. When phosphoric acid and potash were applied with the leather, a slight increase in the yield of grain was noticed, while in case of the dried blood plus the phosphoric acid and potash, the yield was twice that of the unfertilized pot.

(b) *Garden Experiments with Horsebeans.*

The soil was the same as in the previous experiment. Size of plats, 60 sq. meters. The fertilizer applied was leather and nitrate of soda. Nitrogen was applied at the rate of 58.5 lbs. per acre.

RESULTS PER PLAT.

	Stems and pods in kilos.	Beans in kilos.	Beans per acre in kilos.
Unmanured	9,869	1,131	37,700
Leather	12,822	1,178	39,268
Nitrate of soda	11,465	2,035	67,832

It will be observed that the leather produced only a slight increase in the yield of beans.

(c) *Field Experiments with Sugar-beets.*

Same soil as in previous experiments. Each plat measured 1 ar. The fertilizer was applied at the rate of 42¼ pounds of nitrogen, and 528 pounds of phosphoric acid per acre.

RESULTS PER HECTARE.

	Kilos.	Percentage increase over unmanured.
Unmanured	34,830	——
Soluble phos. acid	34,380	—1.5
Water and citrate sol. phos. acid	34,290	—1.2
Citrate sol. phos. acid	34,380	—1.5
Unmanured	33,840	——
Leather + sol. phos. acid	37,890	11.9
Leather + water sol. + citrate sol. phos. acid	37,180	10.7
Leather + citrate sol. phos. acid	35,910	6.0
Unmanured	32,940	——
Nitrate of soda + sol. phos. acid	43,380	28.1
Nitrate of soda + water + citrate sol. phos. acid	42,070	24.2
Nitrate of soda + citrate sol. phos. acid	43,830	29.4

While the leather has shown its effect, it runs far behind the nitrate of soda. Petermann says that from a financial standpoint the leather shows a loss and the nitrate of soda a gain. Of his results the experimenter makes the following resumé:

"With horsebean, the leather shows practically no influence the first year. With oats and sugar beets an increase is noted, but this is slight when compared with that from blood and nitrate of soda." In a later publication, Petermann says that in his experiments from 1880–1885, the various forms of nitrogen have shown the following relative worth: 1. Nitrate of soda; 2. blood; 3. dissolved wool; 4. ground bone; 5. raw wool; 6. leather.

Deherain* gives the results of the following experiments conducted in the field at Grignon with ground leather. The results with wheat in 1880 and 1881, show the residual effect of that applied to potatoes in 1879:

	Potatoes. 1879.	Wheat. 1880.		Wheat. 1881.	
	Hectolitres.	Grain. Qtm.*	Straw. Qtm.	Grain. Qtm.	Straw. Qtm.
Unfertilized	224	25.0	37.25	16 4	20.5
Leather, 2000 kilos	295	27.5	40.00	23.4	38.7
Leather, 1000 kilos	277	25.0	38.00	23	37.6

* Qtm. = quintal metrique = 100 kilograms.

Deherain remarks that his experiments make it clear that the

* *Chimie Agricole* (1892), 619.

leather yields its nitrogen very slowly. He does not state whether the leather used had been steamed, roasted, or was untreated.

Müntz* and Girard, in connection with their experiments on the nitrification of various nitrogen-containing organic substances, carried out also a series of field experiments with various nitrogenous materials. Each plat had an area of one ar. and received 1.25 kilos of nitrogen the first year, together with the necessary quantity of phosphoric acid and potash. No manure was applied the second year. The soil was light and sandy, being quite favorable to nitrification. The plats were planted with fodder corn during both years.

FODDER CORN GROWN UPON ONE AR. (DRY MATTER).

Form of nitrogen.	1888. Kilos.	1889. Kilos.	Average of both years.
Nitrate of soda	143	47	190
Dried blood	130	48	178
Roasted horn	123	52	175
Roasted leather	91	61	152
No nitrogen	59	43	102

The above results show that leather even when roasted is quite inferior in its action to dried blood and nitrate of soda.

Märcker† gives the following results obtained by Seyffert, at Halle, with cole-rape:

Form of nitrogen.		Yield in grammes.
No nitrogen		75.5
No nitrogen	Leather	469
	Steamed bone meal	1,572
	Blood	1,654
	Nitrate soda	2,607.5

In order to control the above experiment another test was carried out with oats by Julius Albert-Münchenhof.

YIELD.

Form of nitrogen.	Grain. Grammes.	Straw. Grammes.	Roots. Grammes.	Total. Grammes
No nitrogen	5.2	15.7	14.3	38.2
Nitrate of soda	48.9	62.6	27.9	139.4
Dried blood	24.8	44.5	18.5	87.8
Leather	13.3	22.2	13.6	49.1
" fermented	21.5	36.4	17.2	75.1

Märcker remarks that leather produced but a slight increase over the unfertilized, and that the quality of the grain was poorest when not any nitrogen was used, or when leather was applied.

* Ann. Agron., 17, 289–304; Biedermann's Centralblatt, **20**, 656.

† Jahresbericht Agr. Chemie, 1883, 241.

Wagner* has made an exhaustive study of the value of different forms of nitrogen, having conducted 366 plat and pot experiments. The experiments were carried on for several successive years in a soil rich enough in lime to favor nitrification, and every effort was made to have the conditions equal in all cases. But a very brief resumè can be given at this time. One experiment was conducted for three successive years upon small plots of soil. Summer rye was planted the first year, summer wheat the second, and carrots the third year. Placing the value of the returns from the nitrate of soda plats at 100, the other forms of nitrogen had the following relative worth :

	1st year.	Average 1st and 2d year.	Average three years.
Nitrate of soda	100	100	100
Blood	67	67	69
Fish	51	59	64
Steamed bone meal	42	53	61
Leather	13	12	20

Experiments were also conducted in pots with various soils, but the results cannot be noticed here.

In concluding his remarks relative to this subject Wagner says, "When I take all things into consideration . . . I think I may present the following figures, as an expression of the relative value of nitrogen in different forms of nitrogen-containing material :

Nitrate of soda	100
Sulfate of ammonia	90
Blood, horn meal and green crops	70
Fine ground bone, fish and tankage	60
Stable manure	45
Wool dust	30
Leather	20

So far as the writer has been able to ascertain, Wagner does not state the form of the leather used.

Taking the price of nitrogen in nitrate of soda at 14.8 cents, a pound of nitrogen in stable manure would be worth 6.7 cents, and in leather 2.8 cents.

NOTE BY THE EDITOR: From this resumè of direct tests of the fertilizer value of leather, the experiments of F. H. Storer (*Bulletin of the Bussey Institution*, **2**, 58–71) should not fail of mention. He tested the manurial effect of sheep-skin and sole-leather. raw and roasted, on several soils in pots, applying various phosphatic and potassic salts in solution. The crop

* *Die Stickstoffdüngung der Landw. Kulturpflanzen*, p. 242.

used was buckwheat. The results were as follows (expressed in weight of total crop in grammes):

	With rain-water.	With sulfate of potash.	With phosphate of potash.	With phosphate of potash and nitrate of lime.
No leather used:				
In Berkshire sand.	0.200	0.200	0.155	0.665*
In Provincetown sand	0.170	——	0.165	3.050
In loam and sand	0.270	——	0.160	5.830
Raw sheep-skin (20):				
In Berkshire sand (1300)....	0.100	0.130	0.055	0.640*
In Provincetown sand (1450)	0.080	——	0.100	1.400
In loam and sand (1320).....	0.170	——	0.120	4.020
Raw sole leather (40):				
In Berkshire sand (1300)....	0.110	0.115	0.120	0.280
In Provincetown sand (1450)	0.120	——	0.110	2.820
In loam and sand (1320).....	0.130	——	0.150	3.720
Roasted sheep-skin (20):				
In Berkshire sand (1300) ...	0.105	0.190	0.060	0.250
In Provincetown sand (1450)	0.250*	——	0 470*	0.345*
In loam and sand (1320).....	0.850	——	0.700	3.060
Roasted sole-leather (40):				
In Berkshire sand (1300)....	0.220*	0.230	0.210*	0.360*
In Provincetown sand (1450)	0.910	——	1.750	3.120
In loam and sand (1320).....	2.120	——	1.980	4.785

* Immature when harvested.

Storer says: "It will be seen plainly enough, that while neither the sheep-skin nor the sole-leather supplied any nitrogenous food to the buckwheat plants, some nitrogen was unquestionably obtained by the plants from the roasted leathers; a little from the roasted sheep-skin and a decidedly larger amount from the roasted sole-leather. . . . In all cases, the light bulky material tended to interfere with the growth of the plants. The roast-leather jars exhibited a marked growth of fungus, the raw leather jars showed none, corroborating the evidence as to the existence of available products in the roast leather. There is but little in the results above given to encourage the belief that roasted leather can have any definite money value as a manure."

(b) *Artificial Digestion Experiments with Leather.*

Stutzer and Klinkenberg* were the first to propose this method. They argued that the amount of nitrogenous material that could be dissolved or digested would give a fairly correct idea of the value of the substance as a source of nitrogen for growing plants. They prepared the digestive fluid by extracting the inner lining of a pig's stomach, cut fiue, with 5 litres of 0.2 per cent. hydrochloric acid for two days, filtering the solution, and preserving in glass stoppered bottles, adding a few grammes of sal-

*Journal für Landw., 1882, p. 365. König's *Vntersuchung Landw. und Gewerblich. Wichtiger Stoffe*, p. 219.

icylic acid to prevent fermentation. They submitted a variety of materials to the action of this solution. A few results are given below:

Substance.	Per cent. of nitrogen digested.
Blood	89.75
Leather (cooked, and then roasted)	39.19
Raw bone	98.70
Steamed bone	90.50

Drs. Shepard and Chazal* afterwards submitted a great variety of nitrogen-containing materials to the action of Stutzer's solution. Several of the results obtained are presented below.

	Per cent. of nitrogen digested.
Roasted leather meal*	37.80
Dried blood (black)	78.61
Fish scrap	88.67

* The author's remark that "this prepared leather was an excellent article, so far as preparation goes, and one capable of being used in the fertilizer trade, without much fear of detection."

Johnson, Farrington and Winton†, instead of using Stutzer's solution, dissolved 5 grammes of Golden Scale Pepsin in 1000 c.c. of 0.2 per cent. hydrochloric acid and digested a variety of substances in this fluid. Their investigation is the most valuable we possess in this direction. A few of their results may be cited.

	Per cent. of nitrogen digested.
Dried blood (two samples)	97.30
Dry ground fish	71.20
Leather No. 3*	23.40
Leather treated by benzine process	35.90
Leather treated by superheated steam	33.30
Mixed fertilizer A containing 2.02 per cent. leather nitrogen	23.40
Mixed fertilizer B containing 200 per cent. leather nitrogen and 1.75 per cent. blood nitrogen	55.60

* Fine and brittle, but method of preparation not known.

In this connection it might be in place to mention the experiments recorded on the putrefaction of ammoniates, at first suggested by A. Morgen.‡ He put leather and horn meal in water to which a small amount of fecal extract had been added, and then allowed the solution to stand for 31 days at 30° C. The nitrogen made solution was then estimated.

* See Report of Conn. Experiment Sta., 1885, p. 117.

† *Loc. cit.*

‡ Landw. Vers. Stat., 1880, **50**; Biedermann's Centralblatt, **9**, 801.

In experiment I=10 grammes material + 1000 cc.m. water were used.
In experiment II=5 grammes material + 1000 cc.m. water + 5 cc.m. fecal extract.
In experiment III, the same with 10 grammes material + 5 cc.m. fecal extract.

	Per cent. of soluble nitrogen.
Leather meal, average of 3 experiments	34.56
Horn meal, average of 3 experiments	61.62

Johnson* repeated Morgen's work on a very large number of substances; a few of the results are given below. He allowed his solution to stand two weeks.

	Per cent. nitrogen soluble.
Blood	76.80
Fish	78.10
Fish	54.60
Bone	79.00
Leather, No. 3	12.20
Steamed leather	42.30
"Prepared ammoniate" (probably leather)	35.70

Johnson remarks that "this test of putrefaction draws the same line between those classes of ammoniates that was drawn by the pepsin digestion."

(c) *Nitrification Experiments with Leather.*

These experiments were carried out by Müntz and Girard† with quite a number of nitrogen-containing substances. They were conducted in the laboratory, and care was taken to see that the soil was properly aired, and that moisture, temperature, etc., were favorable to the experiment. Ordinary soil was at first used, the amount of nitrates present being carefully noted and a small amount of the substances to be nitrified then added. After a certain time, the nitrates were washed out with water and estimated. A very short resumé is here presented:

NITROGEN NITRIFIED, PER 100 PARTS OF NITROGEN ADDED TO THE SOIL.

	I. 30 days.	II. 39 days.	III. 32 days.
Sulfate of ammonia	75	83.76	83.76
Dried blood	72.44	73.56	84.50
Roasted horn	71.03	73.17	46.82
Roasted leather	11.62	16.47	13.26

In order to study the influence of different kinds of soil upon the process of nitrification, the experiment was repeated with soils from various sections of the country.

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* *Loc cit.*

† Ann. Agron. **17**, 290; Agric. Science, **7**, 408–12; Deherain, *Chimie Agricole*, p. 621.

NITRIC NITROGEN FOUND IN DIFFERENT SOILS WITHIN A CERTAIN TIME.

	Light soil of Joinville. Grammes.	Chalky soil. Grammes.	Garden earth. Grammes.	Very heavy limey clay. Grammes.	Marsh soil, sour, Bretagne. Grammes.
Sulfate of ammonia...	2.69	1.78	——	0.51	None
Blood	1.62	.73	——	.036	"
Roasted horn............	1.22	——	1.08	.029	"
Roasted leather.........	0.41	0.24	0.55	.036	"

These experiments in general coincide with field and pot experiments as well as with artificial digestion experiments. It is worthy of note, that the light sandy soil was most favorable to the process of nitrification, while the very heavy clay, and especially the sour marshy soil was decidedly unfavorable to the action of nitrifying organisms.

LEATHER REFUSE—ITS VALUE IN AGRICULTURE.

BY J. B. LINDSEY.

Second Paper.

Notes on Work Done with Leather at the Massachusetts State Experiment Station.

It is desired at this time to refer briefly to some tests carried out by the writer at the above station.

Can leather be identified in fertilizer mixtures?

If one were to depend upon the microscope, it would certainly be an impossibility to recognize leather in finely ground fertilizer

mixtures. Even if material of a fibrous structure were detected, it would be nothing strange, for all flesh presents such a structure. After leather has been submitted to heat or pressure, all structure is destroyed. Able microscopists who have attempted to identify the leather under the microscope, report it an impossibility.

With chemical reagents, one is more successful. At least, tannic or gallic acids, from their well known reaction with an iron salt, are easily recognized, and while one perhaps could not positively declare that the tannic or gallic acids present were derived from leather, it certainly would be highly probable.

Dr. C. W. Dabney,* when director of the North Carolina Experiment Station, published a bulletin in which he suggests that the best reagent for recognizing the tannic acid, is a phosporic acid solution of phosphate of iron. He states that if leather be present in the substance examined, a purple color will soon appear, if a few drops of this solution be added to the alkaline solution of the leather extract. I prepared the phosphoric acid solution of phosphate of iron as follows : Ten grams of ferric chloride were dissolved in water and sodium phosphate added till all the iron was precipitated as phosphate of iron. The phosphate of iron must be freshly prepared, otherwise it will dissolve slowly, if at all. The phosphate of iron was filtered and washed quite thoroughly with water, and both filter and precipitate brought into a beaker containing 400 c.c. of water to which had been added 40 grams of glacial phosphoric acid. A gentle heat dissolves the iron phosphate quite readily.

If a drop of pyrogallic acid is added to water, the solution made slightly alkaline with ammonia, and then a cubic centimeter of the iron phosphate solution added, a dark purple color appears. If tannic acid is substituted for the pyrogallic acid, a dark wine color results. In order to recognize leather in a mixture, a small amount (1 gramme) of the substance supposed to contain it, is placed in a beaker with 30-40 c.c. of water, a few drops of sulfuric acid added, the liquid brought to boiling, filtered, a little of the iron phosphate solution added, and the solution then made slightly alkaline with ammonia. If leather is present, a dark purple to wine color will soon appear.

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*North Carolina Expt. Sta. Bull. No. 3, 1883: Horn, Leather and Wool Waste.

Should leather be present in a mixed fertilizer containing soluble phosphate of lime, the latter will of course be precipitated on the addition of ammonia, but this in no way interferes with the color reaction. The writer examined during the summer of 1893 quite a number of fertilizers officially collected in Massachusetts, but in no case was leather to be detected. When, however, 10 per cent. of leather was added to a mixed fertilizer, and then tested with the phosphate of iron solution, the dark color, due to the presence of tannic or gallic acids very distinctly appeared.

During the early summer of 1893 several samples of leather were received at the station. It was stated that large quantities of the material were on the market, and one could surmise at least that it might be used as a source of nitrogen in the manufacture of commercial fertilizers, organic nitrogen at the time being quite high in price. It was thought wise to submit the samples to several tests, and for the sake of comparison, pure sole leather obtained by the writer at the cobbler's, and dried blood were also included.

Description of the Samples.

I. Sole leather.

This leather was ground fine for future tests. Under the microscope it showed a distinct fibrous structure. It contained 2.76 per cent. of fat and 7.94 per cent. of nitrogen.

II. Steamed leather.

Some of the finely ground leather was placed in pressure bottles, water added, and heated for 6 hours at 110° C. The leather was virtually subjected to three atmospheres of steam pressure. After treatment it had become very dark in color and appeared as a jelly-like, amorphous mass. The microscope showed it to be devoid of any fibrous structure. The tannic or gallic acids were still easily recognized, showing that they had not been destroyed by the heat and pressure. When dry, it became quite brittle, crumbling easily.

III. Coarse leather sent to the station.

This leather came in pieces, from the size of a walnut to that of a small hen's egg. It contained 37.47 per cent. of fat and 4.52 per cent. of nitrogen. The large amount of fat completely concealed its structure.

IV. Philadelphia Tankage.

The sample was very finely ground and quite dry. It contained 1.95 per cent. of fat, 7.80 per cent. of nitrogen and traces only of phosphoric acid. Its smell and general appearance indicated clearly that it was leather that had been roasted or steamed. To the eye it appeared to be lacking in fibrous structure, and with the microscope it appeared simply as a gelatinous mass.

V. Dried blood.

It was an excellent sample, containing 12.71 per cent. of nitrogen and 0.64 per cent. of fat.

Artificial Digestion of Different Leathers.

The artificial digestion of the substances above described was carried out according to Stutzer's method. In the first series of trials both the pepsin and pancreas solutions were used. The preparation of the pepsin solution has already been described.

The pancreas solution was prepared by taking the fresh pancreas of an ox, cutting it fine, mixing it with sand and allowing it to stand 24 to 36 hours exposed to the air. It was then rubbed with lime water and glycerine (to every 1,000 gm. of the pancreas-sand mixture use 3 litres of lime water and one litre of glycerine of 1.23 sp. gr.), and the resulting fluid allowed to stand with occasional stirring for five days. It was then filtered through cloth to remove the coarse portions, heated to 40° C. for two hours, and finally filtered through folded filters, and preserved in bottles. To prepare the pancreas solution used in the process of digestion, 250 c.c. of the above described solution were mixed with 750 c.c. of soda solution. The soda solution contained 5 grammes of carbonate of soda dissolved in 750 c.c. of water. The pancreas solution thus prepared was heated for one to two hours at 37–40° C., filtered to remove any flocky precipitate and one hundred c.c. used for each test.

The results of the pepsin-pancreas digestion were as follows:

		Per cent. of nitrogen digested.
I.	Sole leather finely ground	80.98
II.	Same leather after being heated 6 hours at 110° C. in pressure bottles with water	97.23
III.	Coarse leather (free from fat)	52.00
IV.	Philadelphia tankage	90.64
V.	Dried blood	99.13

The above results are all very high, but this is not surprising, for the action of dilute alkalies on leather is well known and has been several times referred to. In the present case, after the various leathers had been submitted to the pepsin digestion, there appeared to be no very great change either in their appearance or bulk. Blood on the other hand was nearly all dissolved by the pepsin solution. As soon, however, as the leathers were submitted to the action of the pancreas solution a decided change was noted. The solution became quite dark in color and the larger part of the leather went into solution. While this method indicated a greater availability on the part of the sole leather *after it had been submitted to steam pressure* it nevertheless did not give a correct idea of the digestibility and consequent availability of the leather when compared with the dried blood.

The substances were therefore submitted to the action of the pepsin solution alone with results as follows:

		Percentage digestibility of nitrogen.
I.	Sole leather	13.70
II.	Sole leather after steam pressure	34.40
III.	Coarse leather	
IV.	Philadelphia tankage	42.30
V.	Dried blood	97.80

These results coincide very closely with those obtained by other investigators. The sole leather itself proved very indigestible. It is possible that it might have proved somewhat less so if no hydrochloric acid had been added during the digestion.* The sole leather *after* being subjected to the action of the steam pressure had a digestibility of 34.40 per cent., which coincides with results obtained by others for prepared leather as the following samples show:

	Percentage of nitrogen digested.
Leather cooked and roasted (Stutzer)	39.19
Roasted leather meal (Shepard and Chazal)	37.80
Leather by benzine process (Johnson)	35.90
Leather by superheated steam (Johnson)	33.30

While then the action of steam and heat renders the leather somewhat more digestible and probably more available in the soil, it still has a digestibility below 50 per cent. Only the very poorest kinds of animal matter reach this low figure (50). The so called Philadelphia tankage was also below 50 per cent. digestible

* Conn. Exp. Sta., 1886, p. 122.

and may be classified with the steamed or roasted leathers as regards its value. It is to be noted, as before mentioned, that the dried blood was nearly all digested by the action of the pepsin solution and may be regarded as a very excellent standard with which to compare the various leathers.

General Conclusions Relative to Raw, Roasted or Steamed Leather.

The results of the combined experiments in the field and in pots together with artificial digestion experiments, and nitrification experiments, indicate that leather, either raw, roasted or steamed, is a very slow acting form of nitrogen as a source of plant food. It certainly would be fraudulent to sell it in mixed fertilizers as a source of organic nitrogen, and the Masachusetts fertilizer law distinctly forbids it to be thus utilized. Carefully conducted experiments by Wagner give it a relative value of 20, nitrate of soda being equal to 100. From the mass of evidence at our command it would seem that this figure about expresses its relative worth as a direct source of plant food. If it is offered for sale as a fertilizer, it should be sold as leather. When nitrogen in organic matter has a value of 16 to 18 cents per pound, nitrogen in raw, steamed or roasted leather should be worth but 3 to 6 cents per pound.

The Action of Sulfuric Acid on Leather.

Deherain and others suggest that if leather be dissolved in sulfuric acid, its nitrogen will be made as valuable as that in any form of animal matter. No experiments, however, are brought forward to prove such a statement, but it is generally understood that many European manufacturers thus turn leather waste to account. In order to study this question more closely, a number of experiments were carried out by the writer, a few of which are presented below.

Experiment I.

Sixty-five grammes of 50° B. sulfuric acid were heated in a porcelain dish over a waterbath to about 90° C. and 12 grammes of leather gradually added. A dark, thick fluid resulted. Thirty c.c. of water were then added to dilute the thick fluid somewhat,

and bone ash was employed to dry off the resulting semi-fluid mass. One hundred and thirty-six grammes of superphosphate were obtained, which gave no tannic acid reaction.

Experiment II.

To 30 grammes of 50° B. sulfuric acid heated as above described, were added 12 grammes of leather. A dark, thick paste was obtained, to which were added 25 c.c. of water, and 33 grammes of bone ash. Seventy-three grammes of superphosphate were obtained. The reaction of tannic acid was not strong.

Analyses of the two products were made as follows :

	I. Per cent.	II. Per cent.
Moisture	18.03	15.59
Soluble phosphoric acid	14.84	11.80
Reverted " "	.69	1.50
Insoluble " "	1.43	3.38
Total " "	16.96	16.68
Nitrogen	0.70	1.20

Experiments III, IV, V, VI.

The previously described Philadelphia tankage was used in these experiments, and South Carolina floats in place of bone ash. The objects in view were to see (a) how much leather could be used without giving a tannic acid reaction, (b) to note if possible to what extent the leather interfered with the action of the sulfuric acid upon the floats, (c) to notice the approximate percentage of available phosphoric acid and nitrogen resulting, (d) to see if any nitrogen in the resulting superphosphates was soluble in water, (e) to note the amount of nitrogen in the superphosphate artificially digestible by Stutzer's solution. To make this latter estimation (e), 5 grammes of superphosphate were stirred with water, filtered, and washed till the wash water was no longer acid. The portion not soluble in water was treated with pepsin solution.

Experiment III.

To 30 grammes of 50° B. sulfuric acid after heating, previously described, were added 12 grams of Philadelphia tankage. A thick, black dough resulted. It was diluted with 25 c. c. of water, appearing then as a thick black fluid. To this fluid were added 60 grammes of floats. The resulting superphosphate, after

drying in the air for 24 hours, weighed 102 grammes. The tannic acid reaction was quite strong.

Experiment IV.

To 30 grammes of 50° B. acid were added 25 c. c. of water and 70 grammes of floats. The dry superphosphate weighed 101.5 grammes.

Experiment V.

To 30 grammes of 50° B. acid were added 9 grammes of Philadelphia tankage, which resulted in a medium thick paste. Twenty c. c. of water and 48.5 grammes of floats were afterwards added. The dry superphosphate weighed 88 grammes, and gave *no* tannic acid reaction.

Experiment VI.

To 30 grammes of 40° B. acid 9 grammes of Philadelphia tankage were added, resulting in a medium thick paste. This paste was diluted with 20 c. c. of water, and 50 grammes of floats were put in. Seventy-nine grammes of superphosphate were obtained, which gave a strong tannic acid reaction.

These several products were analyzed.

	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.
Moisture	14.14	14.13	14.86	——
Soluble phosphoric acid	6.78	7.30	7.80	——
Reverted " "	1.22	1.60	0.44	——
Insoluble " "	5.50	6.66	4.94	——
Total " "	13.50	15.56	13.18	——
Total nitrogen	0.81	——	0.87	1.03
Nitrogen after artificial digestion	0.37	——	0.25	0.41
Per cent. of total nitrogen digested	54	——	71	60
Soluble nitrogen	trace	——	trace	——

It would appear that 9 grammes of leather were all that could be added to 30 grammes of sulfuric-acid without getting the tannic-acid reaction. When, as in Experiment III., 12 grammes of leather were added, the reaction for tannic acid was quite marked, and the nitrogen in the superphosphate had a digestibility of but 54 per cent. Experiment VI. indicates that 40° B. sulfuric acid was not quite strong enough to thoroughly disintegrate the 9 grammes of leather, for the tannic acid in the superphosphate was easily recognized, and the nitrogen was but 60 per cent. digestible. When 9 grammes of the Philadelphia tank-

age were dissolved in 30 grammes of 50° B. acid, no tannic acid could be recognized, and 70 per cent. of the total nitrogen was digestible. This is probably the average percentage of organic nitrogen that would be found digestible in mixed fertilizer, as offered for sale in our markets. Such a result is quite encouraging. It would seem from the analysis of IV. that the leather had not seriously interfered with the action of the sulfuric acid upon the floats. We have in the four experiments above cited, added rather too much phosphate rock and water, and in the two following experiments, less were added.

Experiment VII.

To 30 grammes of 50° B. acid 9 grammes of Philadelphia tankage were added, and then 12 c.c. of water. To the thick fluid resulting, 41 grammes of floats were added. After standing 24 hours, the material could be easily handled, and weighed 71.5 grammes.

Experiment VIII.

To 30 grammes of 50° B. acid 9 grammes of Philadelphia tankage were added, producing a thick pasty mass. Without the addition of water, 28 grammes of floats were stirred in, and after 24 hours, the mass weighed 63 grammes. The phosphate was quite black in color, and sticky. It needed at least 5 to 7 grammes more floats, before it could be easily handled. It was plain that the sulfuric acid was not all neutralized. If no water were added to dilute the thick pasty mass, it would be very difficult to work in the floats should large quantities be mixed.

ANALYSES.

	VII. Per cent.	VIII. Per cent.
Moisture	17.95	16.95
Soluble phosphoric acid	6.79	5.99
Reverted " "	2.16	1.62
Insoluble " "	1.94	1.56
Total " "	10.89	9.17
Total nitrogen	0.90	1.06

In Experiment VII., 8.95 per cent. of available phosphoric acid was obtained, with but 1.94 per cent. of insoluble acid, and 0.90 per cent. of nitrogen; the phosphate was also in good mechanical condition and gave no tannic acid reaction. The proportions of water, sulfuric acid, floats, and leather, appear to be about correct,

and the percentages of available phosphoric acid and nitrogen as high as could be expected, with floats as a dryer.

Experiment IX.

In Experiments III to VIII Philadelphia tankage was used as a source of leather.

In this experiment, pure, fine ground sole leather was used, to see if the sulfuric acid acted as strongly upon the pure leather, as upon the prepared article. To 30 grammes of 50 B. acid were added 9 grammes of sole leather, 20 c.c. of water, and 60 grammes of floats.

The resulting phosphate weighed 98.5 grammes

Analysis gave the following results :

	Per cent.
Total nitrogen in the superphosphate	0.71
" " after digestion	0.22
" " digested per cent	69.
Nitrogen soluble in water	0.047
Per cent. of soluble nitrogen	6.62

No tannic acid could be detected in this superphosphate. The digestion test was made in triplicate, and showed that the pure sole leather, after treatment with sulfuric acid, was quite as digestible as the steamed or roasted leather after a similar treatment, and as digestible as the average animal matter sold for fertilizing purposes.

In order to still further study the value of dissolved leather as a source of plant food, pot experiments are now in progress at the station, and the results will be reported later.

Practical Deductions.

The various experiments made would indicate that leather, sulfuric-acid, water and floats should be mixed in about the following relative proportions :

2,000 lbs.	50° B. sulfuric acid
600 "	ground leather
800 "	water
2,700 "	floats

The resulting mixture, when in fairly dry condition, would weigh approximately 5,000 lbs., shrinking about 18 to 20 per cent. It would have approximately the following composition :

	Per cent.
Moisture	18.00
Available phosphoric acid	8.50
Insoluble " "	2.00
Total " "	10.50
" nitrogen	0.90

Two thousand pounds of sulfuric acid will not take up more than 600 lbs. of leather and render the leather 70 per cent. digestible. If more is added, part of the latter, whether roasted or raw, will not be thoroughly acted upon by the acid. With 600 lbs. of leather, a thick paste results which must be diluted somewhat with water in order to allow the sulfuric acid to act freely upon the floats. If bone ash should be used as a dryer in place of ground phosphate rock a higher percentage of available phosphoric acid and of nitrogen would result, as Experiments I and II indicate.

Before submitting the leather to the action of the sulfuric-acid, it would undoubtedly be better, after extracting the fat, to steam or roast it, in order that it may be easily pulverized. Raw, untreated leather is ground only with difficulty, and if the mechanical condition of the leather were poor, the action of the sulfuric acid would be imperfect

Resumè—Action of Sulfuric Acid Upon Leather.

Artificial digestion experiments show that the nitrogen in either untreated, steamed or roasted leather after being acted upon by sulfuric acid has a digestibility of 70 per cent. If pot and field experiments corroborate the digestion experiments, it would make plain that the nitrogen in leather after being thus treated would be as available as a source of plant food as the nitrogen in the average fish, blood, etc.

Whether it would be practicable from an economical standpoint to thus utilize the leather waste is of course another question which must be answered by practical experiments.

Mass. State Experiment Station,
April, 1894.